Electronic Supplementary Information (ESI)

Surface Reconstruction Layer Boosting Interfacial Stability of $LiCoO_2/Li_6PS_5Cl$ in Bulk All-Solid-State Li Batteries

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Experimental details

Preparation of the Materials

Xiamen Tungsten Co., Ltd (XTC) supplied the monocrystal $LiCoO_2$. Indium foils (0.05 mm in thickness) were purchased from Tengfeng Metal Materials Technology Co., Ltd. Solid electrolytes (Li_6PS_5Cl (LPSCl)) were purchased from Hefei Kejing Materials Technology Co., Ltd. The reducing gas (CH_4) was purchased from Guangzhou Danoutong Trading Co., Ltd. Lithium (99.99% purity, 50 mm in thickness) was brought from China Energy Lithium Co., Ltd.

Preparation of SR(CH_4)-LCO

The treatment of P-LCO is carried out in a quartz tube furnace. A multi-step thermal method was used to precisely regulate the SRL layer over LCO. The N_2 flux was used as a protective gas during the temperature increase. When the temperature reached 650 °C(5°C/min), the gas was converted to CH_4, and the reduction reaction between CH_4 and LCO was initiated. Following the chilling process, the gas is converted to N_2 protection gas until it reaches room temperature. By adjusting the sintering time, a series of SR-LCO oxides (designated as SR-LCO-X min, where X = 5 and 10 minutes) with various GSIRR reaction times with CH_4 gas were produced.

Electrochemical tests

Using the battery testing system (LAND, Wuhan) at room temperature (25 °C), the galvanostatic discharge/charge tests of ASSLBs with LCO cathodes were carried out at a potential range of 2.6-4.3 V vs. Li+/Li, where 1C was defined as 120 mA g-1. For high voltage test conditions, a potential range of 2.6-4.5 V (or 2.6-4.6 V) vs. Li+/Li was applied, and 1C was defined as 120 mA g-1. The GITT curves of ASSLBs were performed with a 20-minute discharge at 0.1C followed by a 2-hour relaxation. Electrochemical impedance spectroscopy (EIS) of ASSLBs was carried out at the Autolab working station (Wantong, Switzerland) with a frequency range of 3500 Hz to 0.01 Hz and an AC perturbation signal of 5 mV.

Materials characterization

Powder X-ray diffraction (XRD) was performed using a Rigaku Ultima IV with a Cu K radiation source and samples were scanned at a 2θ range of 5 to 90° at a scan speed of 1° min^{-1}. Use a scanning electron microscope (SEM, TESCAN MIRA4) to observe the morphology of cathodes before and after reduction. A high-resolution transmission electron microscope (HRTEM) was used to study the CoO/Li_2CO_3 SRL layer on the surface of LCO at an accelerating voltage of roughly 200 kV. Before TEM observation, thin sections of the $SR(CH_4)$-LCO-5min particles were prepared using the Focused Ion Beam (FIB) technique. Surface components of samples were analyzed using a PHI-5000versaprobeIII electron spectrometer (X-ray photoelectron spectroscopy, XPS), and the binding energies reported herein were corrected for the C-C/C-H signal at 284.8 eV. As an X-ray source, Al Kα monochromatized radiation (hν = 1486.6 eV) was used. The surface of the specimen is sputtered by inert gas ion bombardment with a sputter rate of 15 nm (SiO_2 as standard reference) for each time, and spectra are then collected from the center of an etched area.

Supplementary figures

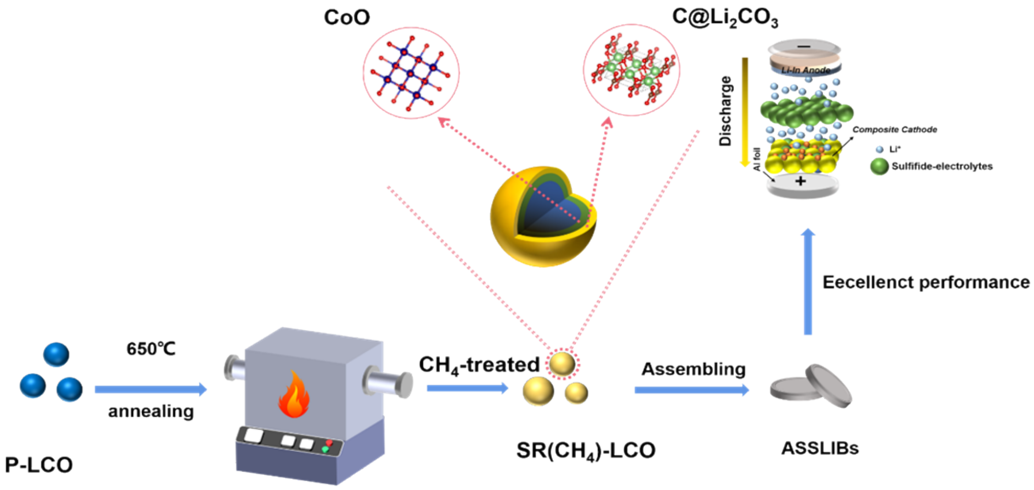

Figure S1 A schematic illustration showing the GSIRR process and the formation of CoO/Li_2CO_3 layer on the surface of the particle.

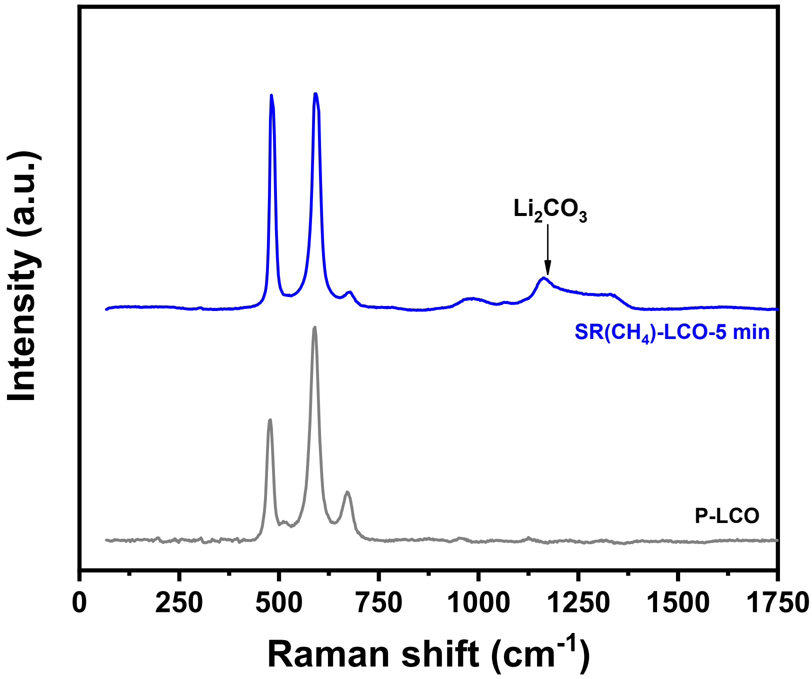

Figure S2 Raman analysis of SR(CH_4)-LCO-5min and P-LCO. The blue trace represents SR(CH_4)-LCO-5min sample. The grey trace represents P-LCO sample.

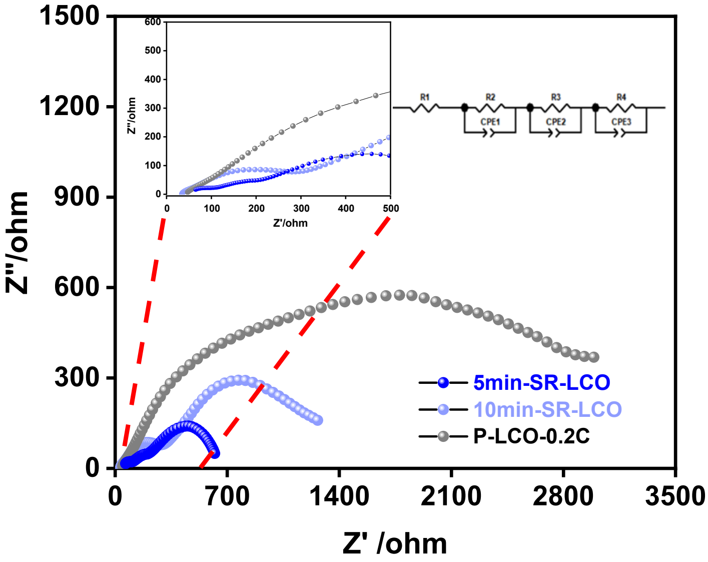

Figure S3 The Nyquist plots of P-LCO, SR(CH_4)-5 min LCO and SR(CH_4)-10 min LCO all-solid-state lithium-ion batteries after 10 cycles at 0.2 C.

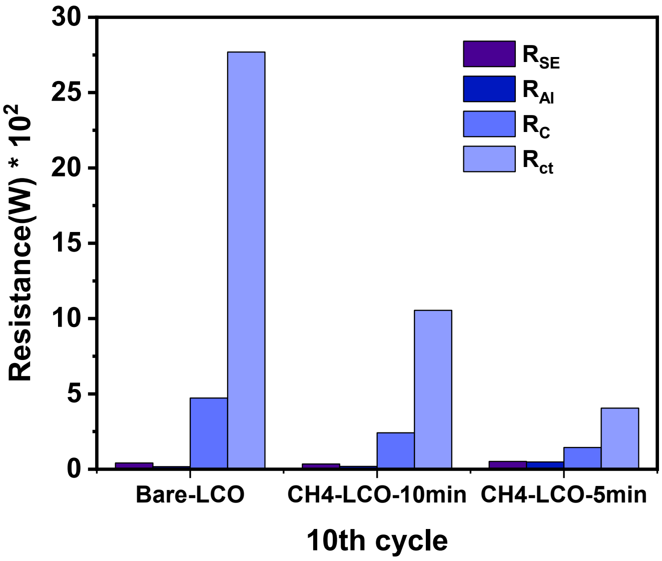

Figure S4 The fitting results of Nyquist plots for batteries.

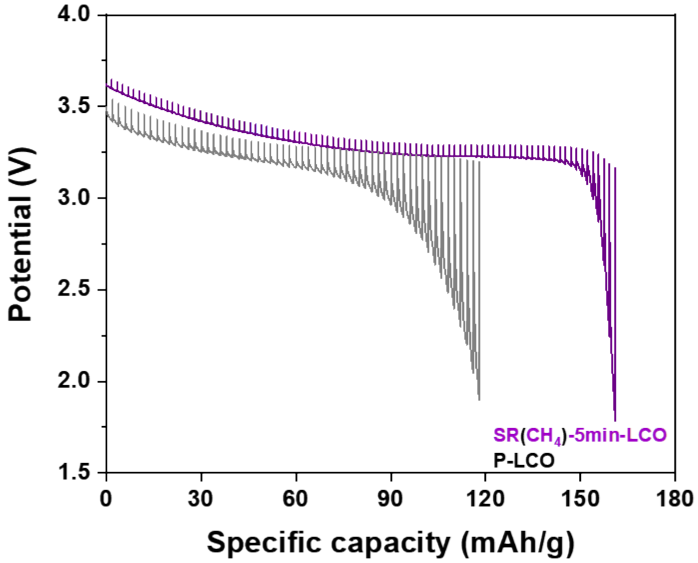

Figure S5 GITT discharge curves of P-LCO and SR(CH_4)-LCO-5 min.

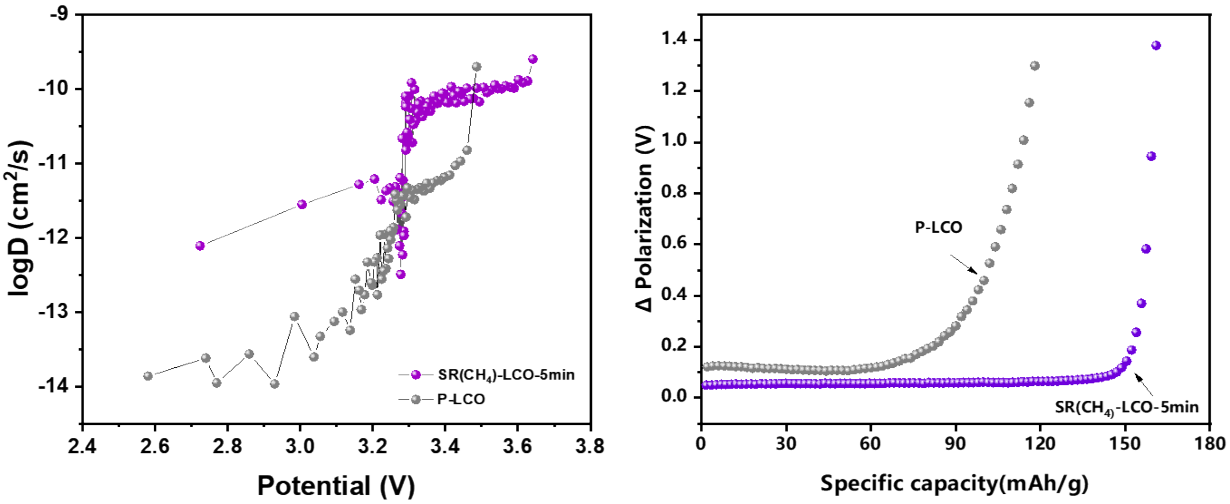

Figure S6 Ion diffusion coefficient log D and Polarization curves of SR(CH_4)- LCO-5 min and P-LCO.

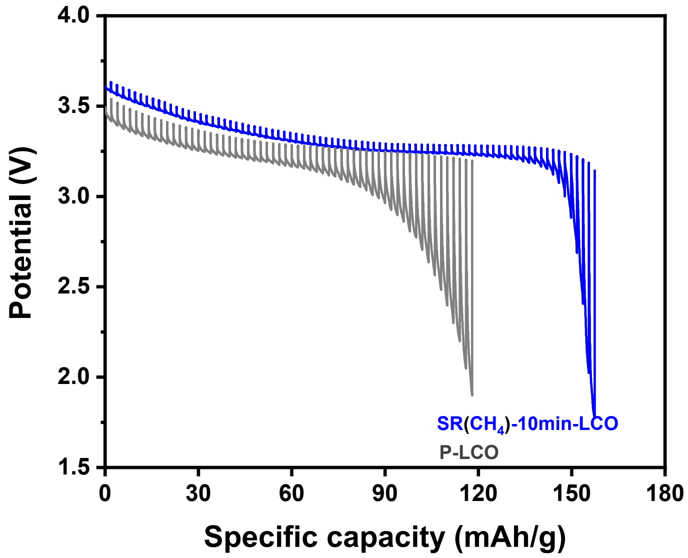

Figure S7 GITT discharge curves of P-LCO and SR(CH_4)-LCO-10 min.

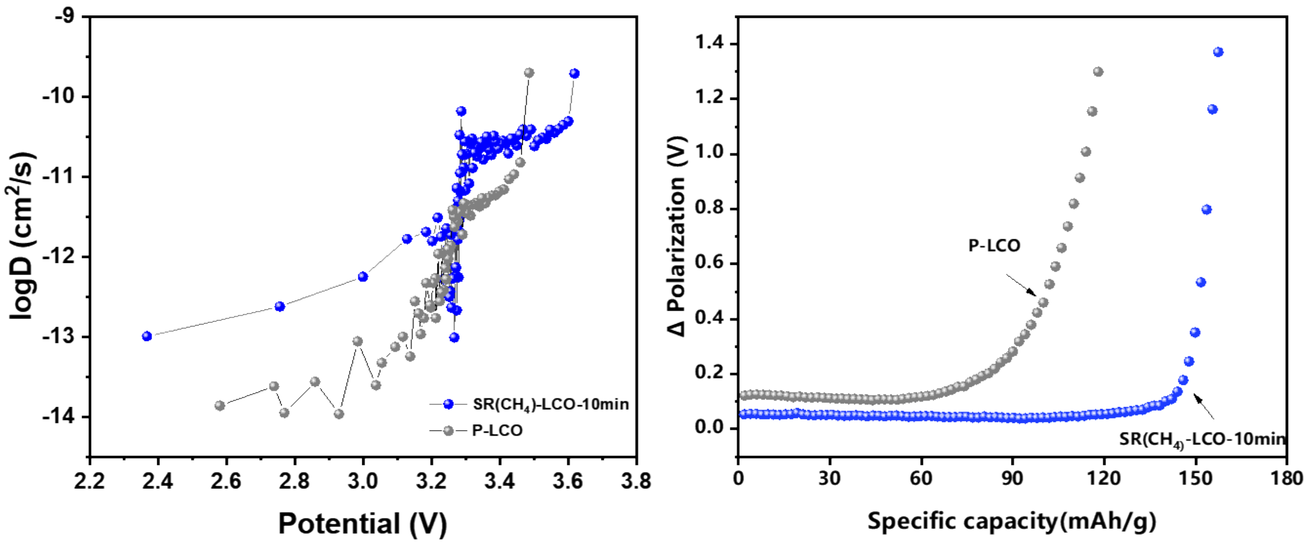

Figure S8 Ion diffusion coefficient log D and Polarization curves of SR(CH_4)-LCO-10 min and P-LCO.

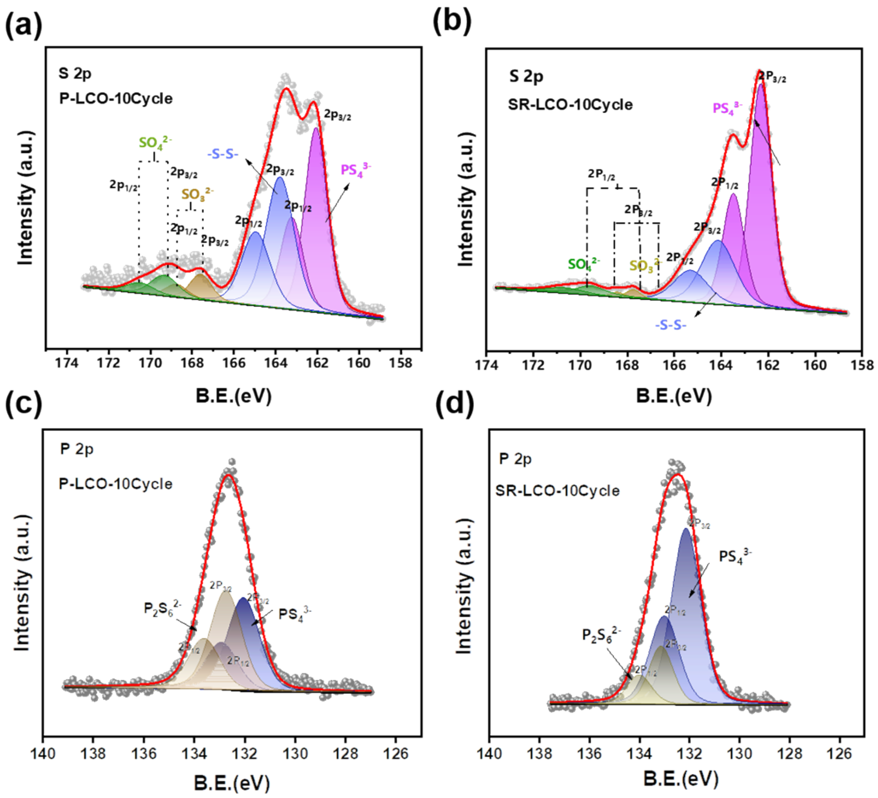

Figure S9 XPS spectra for P-LCO and SR-LCO. (a-b) S 2*p* and (c-d) P 2*p* XPS spectra of P-LCO/LPSCl interface and SR-LCO-5min/LPSCl interface after 10 cycles at 0.2C.

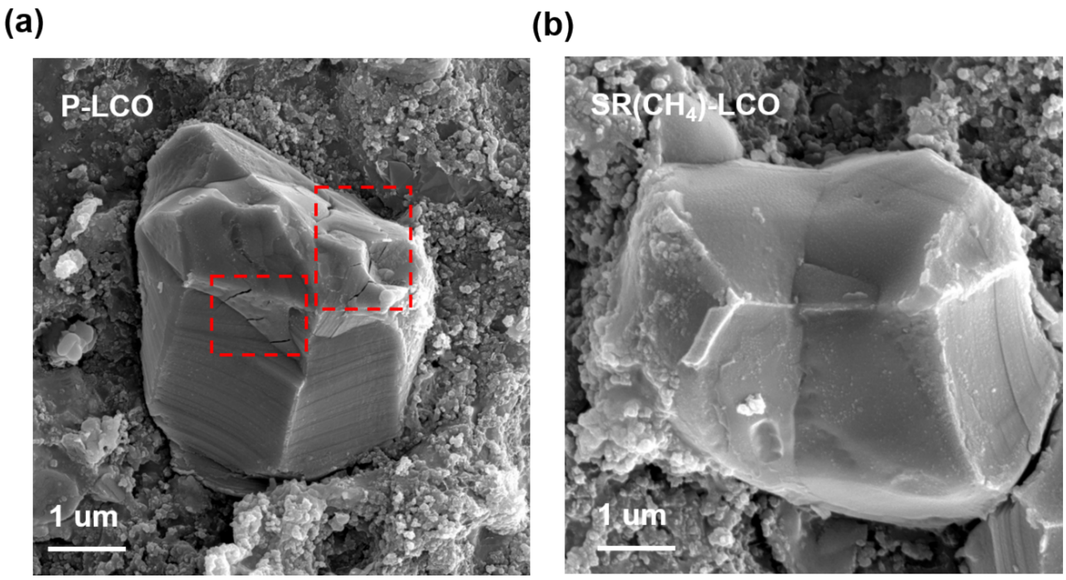

Figure S10 (a-b) The SEM images of P-LCO and SR(CH4)-LCO after 10 cycles at 0.2C.

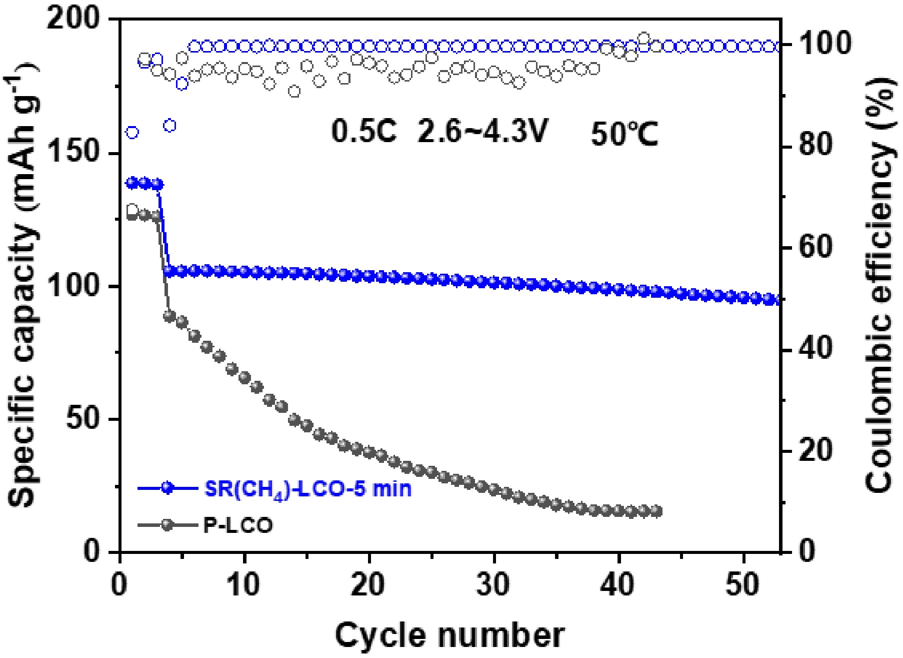

Figure S11 The performance of ASSLBs with SR(CH_4)-LCO-5min and P-LCO at 0.5 C under 50℃.

Table S1 Detailed comparison of the electrochemical performance of different coating in ASSLBs.

	Design in ASSLBs	T (°C)	Voltage Range (V)	Rate	Initial discharge capacity (mAh g^{-1})	Capacity retention (%)	Cycles
This work	CH_4-LCO-5min|LPSCl|In-Li	25	2.6-4.5	0.5C	149.8	89.38	200
	CH_4-LCO-5min|LPSCl|In-Li	25	2.6-4.6	0.5C	168.6	82.68	158
1	$LiNbO_3$@LCO|LGPS|In-Li	25	2.5-4.2	1C	115	81.73	50
2	Al_2O_3/$LiAlO_2$@NCM|LPSCl|In-Li	25	2.6-4.3	0.25C	138.9	54	100
3	Li_3BO_3@LCO|LLZTO|Li	25	2.7-4.2	0.05C	136	76	100
4	$Li_2CoTi_3O_8$@LCO|LGPS|In-Li	30	2.1-4.5	0.2C	180	73.3	100
5	LNO@NCM811|LPSCl|In-Li	30	2.7-4.38	0.5C	162	77.9	50

References

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